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Pyrazole-Based PCN Pincer Complexes of Palladium(II): Mono- and Dinuclear Hydroxide Complexes and Ligand Rollover C-H Activation

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Abstract

© 2015 American Chemical Society. Palladium complexes of the novel unsymmetrical phosphine pyrazole-containing pincer ligands PCN^{H} (PCN^{H} = 1-[3-[(di-t-rt-butylphosphino)methyl]phenyl]-1H-pyrazole) and PCN^{Me} (PCN^{Me} = 1-[3-[(di-t-rt-butylphosphino)methyl]phenyl]-5-methyl-1H-pyrazole) have been prepared and characterized through single-crystal X-ray diffraction and multinuclear ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectroscopy. In preparations of the monomeric hydroxide species (PCN^{H})Pd(OH), an unexpected N detachment followed by C-H activation on the heterocycle 5-position took place resulting in conversion of the monoanionic {P,C^{-},N} framework into a dianionic {P,C^{-},C^{-}} ligand set. The dinuclear hydroxide-bridged species (PCN^{H})Pd(μ-OH)Pd(PCC) was the final product obtained under ambient conditions. The "rollover" activation was followed via $^{31}P\{^{1}H\}$ NMR spectroscopy, and dinuclear cationic μ-OH and monomeric Pd^{II} hydroxide intermediates were identified. DFT computational analysis of the process (M06//6-31G∗, THF) showed that the energy barriers for the pyrazolyl rollover and for C-H activation through a σ-bond metathesis reaction are low enough to be overcome under ambient-temperature conditions, in line with the experimental findings. In contrast to the PCN^{H} system, no "rollover" reactivity was observed in the PCN^{Me} system, and the terminal hydroxide complex (PCN^{Me})Pd(OH) could be readily isolated and fully characterized. (Chemical Equation Presented).

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